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A STUDY OF THE THERMAL DECOMPOSITION OF NITROGEN PENTOXIDE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

by

DOROTHY GETZ

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ACKNOWLEDGMENTS

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She also welcomes this opportunity of acknowledging a special indebtedness to Drs. Frazer and Patrick for their kindness and help.

Thanks are also given to Dr. Thornton for his direction and assistance in work already published in The American Journal of Science, *9*, 176 (1925) and offered in partial fulfillment of the requirements for the degree.

Furthermore, she wishes to heartily thank Drs. Reid, Bichowsky, Urey and Swartz for their kindly assistance and instruction in laboratory and class-room.

A STUDY OF THE THERMAL DECOMPOSITION OF NITROGEN PENTOXIDE[1]

BY DOROTHY GETZ[2]

The field of reaction rate investigation has been very fruitful in producing an extensive literature on the theory of chemical reactivity. Of all reactions, first-order, homogeneous gas reactions are perhaps theoretically the most interesting. From time to time various gaseous decompositions have been reported as unimolecular, but further work has usually shown them to be either heterogeneous or multimolecular. Within the past year, however, several new reactions have been brought forward as unimolecular.[3]

At the time the present investigation was undertaken, the thermal decomposition of nitrogen pentoxide held the unique position of "sole survivor of the group of truly monomolecular reactions".[4] The velocity of this reaction has been measured under a wide variety of conditions, and, with two exceptions, has always conformed to the original values obtained by Daniels and Johnston. The initial pressures of the pentoxide have been varied over wide limits with no effect on the specific reaction rate except in the work of Hirst and Rideal who found a velocity five times the normal value when the total gas pressure was below about .25 millimeters, the rate falling off to normal as the pressure increased due to the decomposition. The effect of the presence of various gases whether inert, such as argon and nitrogen, or whether decomposition products such as oxygen and nitrogen tetroxide, has been studied and the gases found to be without influence on the velocity. However,

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[1] Contribution from the Chemical Laboratory of the Johns Hopkins University.

[2] Extracts from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Hinshelwood and Hutchison: Proc. Roy. Soc., **111** A, 245 (1926); Hinshelwood and Thompson: **113** A, 221 (1926); Hinshelwood: **114** A, 84 (1927); Smith: J. Am. Chem. Soc., **49**, 43 (1927); Ramsperger: **49**, 912 (1927).

[4] It seems desirable to include a bibliography of the experimental work on nitrogen pentoxide. Unmarked citations in the text refer to this list.

(a) Daniels and Bright: J. Am. Chem. Soc., **42**, 1131 (1920). Vapor Pressure.
(b) Daniels and Johnston: Ibid., **43**, 53 (1921). Thermal Decomposition.
(c) Daniels and Johnston: Ibid., **43**, 72 (1921). Photochemical Decomposition.
(d) Lueck: Ibid., **44**, 757 (1922). Thermal Decomposition in Solution.
(e) Wulf, Daniels and Karrer: Ibid., **44**, 2398 (1922) Oxidation of N_2O_4 by O_3. Daniels, Wulf and Karrer: Ibid., **44**, 2402 (1922). Decomposition of N_2O_5 in Presence of O_3.
(f) White and Tolman: Ibid., **47**, 1240 (1925). Initial Rate of Decomposition.
(g) Hunt and Daniels: Ibid., **47**, 1602 (1925). Decomposition at Low Concentration.
(h) Daniels: Ibid., **47**, 2856 (1925). Infra-red Absorption Spectra.
(i) Hirst: J. Chem. Soc., **127**, 657 (1925). Thermal Decomposition.
(j) Hirst and Rideal: Proc. Roy. Soc., **109** A 526 (1925). Decomposition at Low Pressures.
(k) Daniels: J. Am. Chem. Soc., **48**, 607 (1926). Infra-red Radiation and N_2O_5.
(l) H. A. Taylor: Ibid., **48**, 577 (1926). Infra-red Radiation and N_2O_5.
(m) F. O. Rice: Ibid., **48**, 2099 (1926). The Catalytic Activity of Dust Particles.
(m) Fazel and Karrer: Ibid., **48**, 2837 (1926). Photochemical Decomposition.
(o) Norrish: Nature, **119**, 123 (1927). Decomposition of N_2O_5
(p) Busse and Daniels: J. Am. Chem. Soc., **49**, 1257 (1927). Effect of Foreign Gases.
(q) Bodenstein: Z. physik. Chem., **104**, 51 (1923). Decomposition of N_2O_5.

arguments have been advanced for and against autocatalytic activity of the dioxide, the strongest evidence for such an effect being the remarkable retardation of the decomposition of the pentoxide observed by Daniels, Wulf and Karrer in the presence of excess ozone. Their experimental results have not been confirmed by other workers.

In view of the theoretical importance of the reaction, of the fact that all other so-called unimolecular reactions up to that time had been found to be heterogeneous or multimolecular on rigorous investigation, and particularly in view of the very interesting results of Daniels, Wulf and Karrer, it seemed worth while to undertake another study of the reaction. Hence we decided to investigate the thermal decomposition of nitrogen pentoxide from two standpoints, namely, (1) the reaction may be heterogeneous; (2) the reaction may be homogeneous but multimolecular, involving a catalyst.

The effect of dust in promoting both the thermal and the photochemical decomposition of hydrogen peroxide has been experimentally demonstrated in this Laboratory.[1] It seemed possible that this reaction might also be due to the catalytic effect of dust—in this case possibly phosphorus pentoxide dust. A survey of the literature lends weight to this hypothesis, since, as far as one can judge from the experimental details given by Wulf, Daniels and Karrer, phosphorus pentoxide dust was probably absent to a far greater extent in their work than in any other. Further, their experiments are the only ones showing any inhibition of the decomposition of nitrogen pentoxide, an inhibition which at the present time is still unexplained. Consequently we tried both to remove dust from the gases entering the decomposition chamber, using asbestos and electrical filters, and to add dust by placing phosphorus pentoxide directly in the decomposition tube.

On the other hand, if the decomposition of nitrogen pentoxide is due to the presence of some catalyst, that catalyst must be some compound which is present in constant amount since widely separated groups of investigators working under different conditions have in general obtained consistent unimolecular constants. Since phosphorus pentoxide has been almost universally used for the preparation of nitrogen pentoxide or for drying purposes, it might be a possible source of some positive catalyst. Further, there is the possibility of nitric acid itself being the catalyst. Since theoretically no reaction goes to completion, there must always be a trace of nitric acid present when the pentoxide is prepared or dried in the usual way. By drying the nitrogen pentoxide at different temperatures such an effect would be revealed since the equilibrium concentration of the nitric acid would be changed. Another method of testing for the presence of an accidental trace of catalyst is to prepare the nitrogen pentoxide by an entirely new method such as from the action of chlorine on silver nitrate; by following this method we eliminated altogether the use of phosphorus pentoxide in the preparation of nitrogen pentoxide.

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[1] Rice and Reiff: J. Phys. Chem., **31**, 1300; Rice and Kilpatrick: 1400 (1927).

Experimental

The nitrogen pentoxide used throughout most of the work was prepared from nitric acid obtained by distilling under a partial vacuum a mixture of four parts of concentrated sulphuric acid with one part of concentrated nitric acid. This practically 100% nitric acid was then dehydrated by means of phosphorus pentoxide and the crude nitrogen pentoxide distilled off and dried completely by distillation back and forth through phosphorus pentoxide as often as necessary.

In the experiments on the decomposition of gaseous nitrogen pentoxide the method of Hunt and Daniels was followed although there were certain modifications in the apparatus. The reaction tube was about 1 cm. in diameter and about 87 cm. in length. This tube was kept at constant temperature very efficiently by using a specially constructed double-jacketed condenser through which circulated the vapors from boiling methyl alcohol contained in a distilling flask. A return tube rendered the heating system automatic. The condenser was carefully wrapped in asbestos to exclude light and minimize heat losses. Two thermometers, one inserted at each end of the condenser, gave a constant check on the temperature.

Several experiments were carried out in the usual way in order to have a check on the results obtained when the filters, etc. were introduced into the system. A stream of nitrogen after passing through drying towers and a flowmeter, entered the tube containing the nitrogen pentoxide which was protected with phosphorus pentoxide guard tubes and kept at 0°C. The resulting mixture of gases streamed through one of these guard tubes cooled with ice, into the decomposition chamber and thence through two test tubes containing standard sodium hydroxide. The results were as follows:

TABLE I

Ordinary Runs on the Decomposition of N_2O_5*

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calculated to 65°C.
1.	.002347	.001018	2.123	64.4	.286
2.	.002402	.001015	2.120	64.4	.276
3.	.002193	.000977	2.194	64.6	.281
4.	.002165	.000967	2.193	64.6	.282
5.	.001948	.000937	2.471	64.5	.281
6.	.001979	.000948	2.467	64.5	.279

*Daniels and Johnston obtained .286 for the calculated value of the velocity constat at 65°C. and .292 for the observed.

We first tried to remove dust from the nitrogen pentoxide by means of asbestos filters. After preliminary experiments we decided to use South African blue asbestos according to the directions of Scott.[1] A filter was prepared from some blue asbestos wool and sealed to the apparatus between the reaction tube and the phosphorus pentoxide guard tube. Two runs were made, but no change in the velocity constant was effected.

[1] Scott: J. Ind. Eng. Chem., **14**, 432 (1922).

TABLE II

Runs using a Blue Asbestos Filter

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C	Observed k calculated to 65°C.
1.	.002115	.000944	2.269	64.5	.282
2.	.001993	.000901	2.226	64.5	.286

An electrical filter was next constructed.[1] The filter resembled a small sealed-in Pyrex condenser. The inner central tube carried the high-tension wire which was made of three lengthwise strands of copper wire from copper gauze with the crosswise strands cut very close, the whole being given several axial turns throughout its length. The outer jacket was provided with inlet and outlet tubes for the pentoxide and was wrapped with copper gauze and grounded. The filter was operated by an induction coil. In preliminary distillations in a current of oxygen no perceptible decomposition was observed qualitatively during the passage of the nitrogen pentoxide through the filter. Several experiments were carried out with the electrical precipitator sealed to the reaction tube. The nitrogen pentoxide was contained in a small tube without phosphorus pentoxide guard tubes. A current of oxygen was used in these experiments. No change in the velocity constant was observed.

TABLE III

Runs using an Electrical Precipitator

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calc. to 65°C.
1.	.002109	.000934	2.435	63.9	.271
2.	.001943	.000911	2.474	64.0	.285
3.	.001947	.000898	2.472	64.0	.279

Another set of experiments was then carried out with the apparatus arranged as originally described, only in these phosphorus pentoxide was introduced directly into the decomposition tube. On the one hand, in all these experiments we had large quantities of dust directly in the reaction tube; on the other hand, we certainly had any catalyst present which might be connected with the use of phosphorus pentoxide, but we could detect no specific effect, even though here the pentoxide was at 65° C. and in preceding experiments in which guard tubes were used the phosphorus pentoxide in the guard tube leading to the decomposition tube had been kept at some temperature between room temperature and 0°C. by partially cooling the tube with ice. The results are given in the table below.

We thought it would be interesting to see if a platinum surface in the reaction tube would have any effect. Consequently several platinum foil electrodes with wires attached were distributed throughout the length of the decomposition chamber. No alteration in the velocity constant was obtained.

[1] See Lamb, Wendt and Wilson: Trans. Am. Electrochem. Soc., **35**, 357 (1919); Tolman, Reyerson, Brooks and Smyth: J. Am. Chem. Soc., **41**, 587 (1919).

TABLE IV

Runs with Phosphorus Pentoxide in the Reaction Tube

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calc. to 65°
1.	.001778	.000817	2.488	64.1	.272
2.	.001718	.000791	2.492	64.1	.273
3.	.002243	.001066	2.454	64.3	.287
4.	.002296	.001099	2.453	64.3	.284
5.	.002241	.001038	2.485	64.1	.276
6.	.002221	.001029	2.488	64.1	.276

TABLE V

Runs with Platinum Electrodes in the Reaction Tube

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C	Observed k calc. to 65°C.
1.	.002237	.001073	2.471	64.4	.282
2.	.002277	.001081	2.468	64.4	.279

Nitrogen pentoxide was next prepared in a different way, eliminating phosphorus pentoxide entirely.[1] The crystals were made by passing chlorine over silver nitrate, a method which was essentially that of Deville[2] though certain modifications were introduced.

The apparatus was arranged as follows. A three-way stopcock leading from nitrogen and chlorine cylinders was sealed to a series of three large U tubes containing glass beads and concentrated sulphuric acid. A trap was placed between these drying tubes and two U tubes containing pulverized silver nitrate sifted over glass beads. These were followed by a filter of glass wool, a tube for collecting the crystals, a similar tube used as a trap and two more large U tubes containing glass beads and concentrated sulphuric acid. Both tubes containing silver nitrate were heated for about two hours by oil baths kept at about 150°C., a current of nitrogen passing through the apparatus meanwhile. The crystals of pentoxide formed when chlorine was slowly passed over the silver nitrate were collected in a tube chilled by ice and salt. It was found necessary to heat the tubes to a rather high temperature to start the reaction and then to hold the temperature around 60°C. After the reaction was completed oxygen dried by passing through concentrated sulphuric acid and an empty tube chilled with carbon dioxide snow and ether, was swept over the crystals. By regulating the temperature at which the crystals were kept, all of the yellow liquid in the tube with the pentoxide was eventually volatilized, and the crystals themselves were then distilled into the next tube which had not been needed as a trap. Part of the time an oxygen current containing a very small amount of ozone was used. The crystals were white and well-formed.

[1] We wish to thank Dr. J. C. W. Frazer for suggesting and helping with this experiment.

[2] Deville: Ann. Chim. Phys. (3) **28**, 241 (1850).

Several runs were made with these crystals. Calcium chloride towers, concentrated sulphuric acid and an empty tube surrounded by carbon dioxide snow and ether sufficed to dry the oxygen or nitrogen used, since all phosphorus pentoxide was carefully eliminated. The velocity constants, however, were the same.

TABLE VI

Runs on Nitrogen Pentoxide prepared from Silver Nitrate and Chlorine

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calculated to 65°C.
1.	.001933	.001061	2.870	64.4	.296
2.	.001939	.001034	2.868	64.4	.284
3.	.001905	.001033	2.873	64.4	.290
4.	.001873	.001024	2.878	64.4	.293

It is quite certain that a little moisture reached the crystals due to some mishaps in sealing the tubes together, etc., but it seems hardly possible that chance would introduce exactly the same amount of nitric acid as might have been present in the preceding work when phosphorus pentoxide was used in the preparation and drying of the crystals. Moreover, oxygen dried as described above, was swept through the apparatus for some time before the measurements were made. Of course the merest trace of nitric acid might suffice to serve as a catalyst. However, the crystals were next distilled directly into phosphorus pentoxide prepared by the method of Finch and Fraser.[1] Before making the following runs the nitrogen pentoxide was distilled into the usual crystal-collecting tube equipped with phosphorus pentoxide guard tubes. Moreover, the decomposition tube had similar guard tubes sealed to each end. The velocity constants remained the same.

TABLE VII

Runs on Nitrogen Pentoxide after Treatment with Phosphorus Pentoxide

Expt.	Mols N_2O_5 Taken	Mols N_2O_5 Decomposed	Time Min.	T°C.	Observed k calculated to 65°C.
1.	.001887	.001058	2.887	64.6	.298
2.	.001834	.001011	2.876	64.7	.288
3.	.001812	.001024	2.877	64.7	.299
4.	.001996	.001026	2.598	64.7	.287
5.	.001976	.000991	2.603	64.7	.276

Decomposition in Solution.

Lueck first investigated the velocity of the decomposition of nitrogen pentoxide in solution. He discovered the remarkably interesting fact that the rate in carbon tetrachloride and in chloroform closely approximates that found by Daniels and Johnston in the gas phase. The only measurements made on the decomposition of the pentoxide in solution naturally have been carried out in organic solvents. We thought it would be very interesting to

[1] Finch and Fraser: J. Chem. Soc., 129, 117 (1926).

see what would happen in 100% nitric acid itself provided the 100% nitric acid should be sufficiently stable under experimental conditions to render only a comparatively negligible correction necessary.

The method of attack planned consisted in running two samples on the nitric acid—nitrogen pentoxide solution. One was to be carried to complete decomposition at a temperature of 65° C., the other to approximately half-life at 35° C. Each sample was to be analyzed for nitrite content, which would give all the necessary data for calculation of the velocity constant after applying one correction for the nitrite originally present in the sample and another for any decomposition of the nitric acid itself. Such decomposition would, of course, not only increase the nitrite content of the sample, but also continually change the concentration of the pentoxide.

This method was successfully applied to a solution of nitrogen pentoxide in carbon tetrachloride. A sample of Eastman's best-grade carbon tetrachloride was introduced into a tube which was then sealed off at the inlet end. The tube was sealed to a long tube of phosphorus pentoxide which was in turn connected with a receiver carrying phosphorus pentoxide guards and a separate inlet tube through which samples could later be withdrawn. After chilling the contents of the distilling vessel with ice and salt, the whole system was evacuated. By then keeping the receiver in ice and salt and the distilling vessel at room temperature the distillation proceeded very slowly and quietly. The receiver was then sealed to a tube provided with phosphorus pentoxide guards and containing nitrogen pentoxide crystals. The nitrogen pentoxide was introduced into the carbon tetrachloride by sending a nitrogen stream through the flowmeter system and over the crystals at 0°C.

A sample of the solution was drawn up into the decomposition vessel and the inlet sealed off. The decomposition vessel consisted of a piece of capillary tubing bent in the form of a U. Just above the bend in one arm of the U a bulb of approximately 1 or 2 cc. capacity had been blown. At some distance above the bulb this arm was bent twice at right angles and drawn out to a long slender delivery tube which was immersed in acidified standard potassium permanganate solution contained in a test tube. The other shorter arm of the U was similarly bent and drawn out in order to facilitate the filling of the tube and the delivery of the sample for analysis after heating. One sample was carried to complete decomposition by heating for twenty or twenty-five minutes in the vapor of boiling methyl alcohol. A second sample was heated to approximately one-half decomposition in the vapor of boiling ether. Some nitrogen dioxide always escaped from the bulb at 35°C. and a great deal came over at 65°C. rendering the test tube guard absolutely essential. A third sample was analyzed for nitrite originally present.

The constant in the first experiment may be slightly low because no such escape of nitrogen dioxide as actually took place was expected, and probably a little dioxide was lost. The constants obtained by using this method were found to agree with those of Lueck's. If, instead of determining the initial concentration of nitrogen pentoxide by permanganate titration of the totally decomposed sample, a total acidity was run on an unheated sample,

the constants approached the calculated value of Daniels and Johnston. One possible explanation of the discrepancy is loss of pentoxide as well as dioxide from the decomposition tube. However, these results are quite interesting considering the simple rough and ready method.

TABLE VIII

Decompostion of Nitrogen Pentoxide in Carbon Tetrachloride

Expt.	Mols N_2O_5 originally present per g. soln.	Mols N_2O_5 decomposed per g. soln.	Time of heating in Min.	T°C.	Observed k calculated to 35°C.**
1.	.0000854	.0000438	90	34.4	.00867
2.*	.0000886	.0000367	77.2	34.2	.00772
3.*	.0000886	.0000444	105	34.2	.00737
4.	.0000718	.0000352	75	34.5	.00961
5.	.0000718	.0000423	105	34.5	.00905
6.*	.0000829	.0000352	75	34.5	.00788
7.*	.0000829	.0000423	105	34.5	.00758

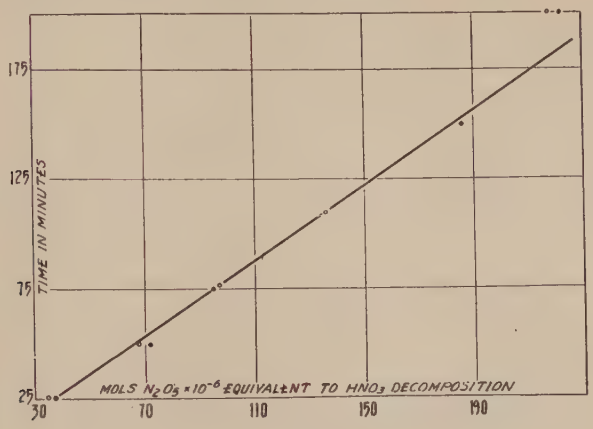
*Average total acidity determined by titration with standard alkali.

**Lueck's value = .00972. Daniels' and Johnston's value = .00808 (observed); .00790 (calculated).

Final results have not yet been obtained on the solutions of nitrogen pentoxide in nitric acid. Some preliminary experiments on the decomposition of nitric acid itself were carried out by heating the acid for twenty-five or thirty minutes at the temperature of boiling methyl alcohol. These were followed by trial runs on two different solutions of nitrogen pentoxide in nitric acid. The results pointed to a much slower reaction velocity than normal; in fact, less than one-tenth of the expected decomposition at 35°C. occurred. This suggested that experiments should be carried out at 65°C. for varying periods of time. Measurements were made on the decomposition occurring during intervals of from twenty-five to two hundred minutes. In the second solution which contained roughly 3% nitrogen pentoxide, the reaction velocity was calculated to be approximately .022 instead of the .286 of nitrogen pentoxide itself. During these runs the experimental method was being worked out, the temperature coefficient of the apparently different reaction is not known, also the concentration of nitrogen pentoxide was quite small which resulted in the decomposition due to nitric acid being a disproportionately large part of the total decomposition, consequently it is hardly possible to give any more definite quantitative data at present.

However, the figures on the decomposition of nitric acid are of interest. In the curve, shown on the graph in Fig. 1, the triangles represent the decomposition of approximately 99.7% nitric acid at 64.9°C., and the circles that of nitric acid which was probably very nearly the same concentration and at temperatures ranging between 64.4 and 64.6°C.

No explanation of the apparently increased stability of nitrogen pentoxide in nitric acid has been tested as yet, but the possibility of compound formation[1] between the two might be suggested and should be investigated by means of a freezing-point composition diagram.



Summary

1. No evidence has been obtained pointing to the decomposition of nitrogen pentoxide being a dust reaction. Apparently there is no catalyst for the reaction connected with the use of phosphorus pentoxide in the preparation and drying of nitrogen pentoxide, since the velocity constants remained the same when phosphorus pentoxide was obtained from different sources or was dispensed with altogether.

2. If nitric acid is a catalyst for the reaction, we have not yet been able to demonstrate it. In the course of attempts to do so, we have found that nitrogen pentoxide appears to be much more stable in 100% nitric acid than in the gas phase or in solution in organic solvents. Possibly this is due to formation of some compound.

3. It is of interest to note that Lueck's figures on the decomposition of the pentoxide in carbon tetrachloride solution have been confirmed by a simple and entirely different experimental method.

Baltimore, Md.

[1] Weber: J. prakt. Chem., **114**, 342 (1873); Veley and Manley: Proc. Roy. Soc., **69**, 86 (1901); Veley: Trans. Faraday Soc., **7**, 229 (1911).

BIOGRAPHY

The author was born in Baltimore, Md., and received her elementary and secondary education in the public schools of this city. In 1917 she graduated with the A.B. degree from Goucher College.

From 1917-1919 she was employed as an Assistant Chemist by the Davison Chemical Company, Curtis Bay, Md. From 1919-1921 she held the position of Assistant in the Chemical Department of Goucher College, and that of Instructor in 1921-1922.

From the spring of 1922 to the present time she has been part time and full time student in the Chemical Department of Johns Hopkins University, holding the position of Student Assistant in the year 1923-1924.